

# Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale watershed, Colorado

T. J. Sullivan,<sup>1</sup> B. J. Cosby,<sup>2</sup> K. A. Tonnessen,<sup>3,4</sup> and D. W. Clow<sup>5</sup>

Received 11 June 2004; revised 21 October 2004; accepted 30 November 2004; published 29 January 2005.

[1] We evaluated the sensitivity of The Loch, a subalpine lake in Rocky Mountain National Park in Colorado, to acidification in response to increased atmospheric loading of sulfur (S) and nitrogen (N) using the Model of Acidification of Groundwater in Catchments (MAGIC). Lake water acid-base chemistry was moderately sensitive to changes in both S and N deposition. However, the loads of S deposition that would drive chronic lake water acid neutralizing capacity (ANC) to below 0 or 20  $\mu\text{eq L}^{-1}$  were estimated to be 11 and 8 kg S  $\text{ha}^{-1} \text{yr}^{-1}$ , respectively, assuming constant future N deposition at current levels. Comparable loads for N deposition, assuming constant future S deposition, were estimated to be 21 and 12 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ , respectively. Modeling results for Andrews Creek, an alpine tributary to The Loch, suggested critical loads for surface water acidification that averaged about one third lower. Surface water ANC = 50  $\mu\text{eq L}^{-1}$  was projected to occur in 50 years in The Loch if S or N deposition increased by a moderate amount (<40%) but could not be achieved in Andrews Creek by reducing either S or N deposition to zero. On the basis of the results of synoptic surveys of lake water chemistry, about one fifth of the wilderness lakes in the Colorado Front Range are more acid-sensitive than The Loch. This modeling exercise suggests the need for a regional analysis of critical loads for the larger population of acid-sensitive aquatic resources in order to provide part of the scientific foundation for federally mandated land management decisions.

**Citation:** Sullivan, T. J., B. J. Cosby, K. A. Tonnessen, and D. W. Clow (2005), Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale watershed, Colorado, *Water Resour. Res.*, 41, W01021, doi:10.1029/2004WR003414.

## 1. Introduction

[2] Atmospheric emissions of sulfur (S) and nitrogen (N) outside national park and wilderness area boundaries in the western United States threaten the ecological integrity of sensitive ecosystems. Aquatic and terrestrial resources, particularly those at high elevation, can be degraded by existing or future pollution. The National Acid Precipitation Assessment Program [*National Acid Precipitation Assessment Program*, 1991] concluded that many high-elevation western lakes were extremely sensitive to acidic deposition effects. The absence of evidence of chronic acidification was attributed to the low levels of acidic deposition received by western watersheds.

[3] Previous acidification research has focused attention on aquatic receptors in the Front Range of Colorado. Although deposition of atmospheric pollutants is generally low [*Sisterson et al.*, 1990], increasing development adja-

cent to protected areas has contributed to increasing air pollution. There are currently elevated emission levels of both S and N adjacent to Rocky Mountain National Park, and elsewhere along the eastern slope of the Front Range [*Heuer et al.*, 2000].

[4] The Clean Air Act (42 USC 7470), as amended in August 1977, provides one of the most important mandates for protecting air resources in Class I areas, that is national parks over 6000 acres and national wilderness areas over 5000 acres. In section 160 of the Act, Congress stated that one of the purposes of the Act was to “preserve, protect, and enhance the air quality in national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value.” To maintain healthy ecosystems, it is increasingly imperative that land managers be prepared to monitor and assess levels of atmospheric pollutants and ecological effects. Knowledge of emissions inventories, coupled with scientific understanding of dose-response functions and critical loads, will provide land managers with a framework to protect sensitive resources within the Class I areas from degradation due to atmospheric deposition of pollutants.

[5] Air quality within Class I lands is subject to the “prevention of significant deterioration (PSD)” provisions of the Clean Air Act. The primary objective of the PSD provisions is to prevent substantial degradation of air quality and yet maintain a margin for industrial growth.

<sup>1</sup>E&S Environmental Chemistry, Inc., Corvallis, Oregon, USA.

<sup>2</sup>Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia, USA.

<sup>3</sup>National Park Service, Air Resources Division, Denver, Colorado, USA.

<sup>4</sup>Now at School of Forestry, University of Montana, Missoula, Montana, USA.

<sup>5</sup>U.S. Geological Survey, Denver, Colorado, USA.

An application for a PSD permit from the appropriate air regulatory agency is required before construction of a new, or modification of an existing, major air pollution source [Bunyak, 1993]. The role of the federal land manager (FLM) is to determine if there is potential for additional air pollution to cause damage to a sensitive receptor. The FLM can recommend denial of a permit by demonstrating that there will be adverse impacts in the Class I area or recommend options for mitigation.

[6] Acidic deposition has the potential to damage sensitive terrestrial and aquatic ecosystems through acidification (S, N) and/or nutrient (N) enrichment. Adverse acidification impacts to surface water include depletion of the acid neutralizing capacity (ANC), reduction of pH, and increased concentration of inorganic aluminum in solution. Such changes in water acid-base chemistry can affect the survival of aquatic organisms. Similarly, nutrient additions can alter aquatic ecosystem structure and function, in part by favoring the growth of some species over others. FLMs need to assess the levels of atmospheric deposition at which such changes occur so as to ensure the protection of sensitive resources. This study focused on acidification effects; nutrient enrichment effects are not explicitly considered. Critical loads for acidification may be different than those for nutrient enrichment.

[7] Public policy measures to reduce emissions of S and N must be based upon quantified dose/response relationships which reflect the tolerance of natural ecosystems to inputs of atmospheric pollutants. This need has given rise to the concepts of critical levels of pollutants and critical loads of deposition [e.g., Bull, 1992], as well as interest in evaluating the efficacy of establishing standards for acid deposition [U.S. Environmental Protection Agency, 1995]. A critical load can be defined as a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge [e.g., Nilsson, 1986; Gundersen, 1992].

[8] It is important for FLMs and regulatory agencies to determine critical loads of S and N that will protect aquatic resources in headwaters and high-elevation watersheds against adverse chemical and biological changes for the following reasons: (1) N deposition has been increasing at many western locations, including the Front Range of Colorado, during recent years [Heuer et al., 2000]; (2) FLMs are faced with an ongoing, and in some locations accelerating, need to provide recommendations for approval or denial of permits for increased point source emissions of S and/or N upwind of sensitive national parks and wilderness area receptors; and (3) mounting evidence suggests that adverse impacts to aquatic resources may be occurring in some Class I areas [Williams and Tonnessen, 2000].

[9] The objective of the work reported here is to evaluate the sensitivity of low-ANC surface waters to acidification from increased S and N deposition. Loch Vale watershed was chosen for modeling due to the large amount of data available for the watershed and its associated waters: The Loch, Andrews Creek, and Icy Brook. Of these, The Loch is least sensitive to acidification because of its position further from the headwaters [Campbell et al., 2000]. We applied the MAGIC model to estimate the acidification responses of The Loch and Andrews Creek to different loadings of S and

**Table 1.** Selected Physical Characteristics of The Loch, Andrews Creek, and Their Respective Watersheds

	The Loch	Andrews Creek
Lake area, ha	5.0	1.3
Lake volume, m <sup>3</sup>	61,000	13,000
Watershed area, ha	690	184
Soil area, ha	55	18
Nonvegetated area, ha	630	165
Terrestrial area draining through soils, %	25	10
Precipitation, cm	117	117
Evapotranspiration, %	28	15

N in deposition. Effects of higher NO<sub>3</sub><sup>-</sup> concentrations on the trophic state and diatom species composition of The Loch [cf. Baron et al., 2000] are not addressed.

## 2. Methods

### 2.1. Site Description

[10] Rocky Mountain National Park is situated along the Colorado Front Range 80 km northwest of Denver. It contains a diversity of ecosystems associated with steep elevational gradients, topographic variation, and differences in climate. Atmospheric deposition of N and S in snow and rain along the northern Front Range is among the highest of any area in the Rocky Mountains [Turk et al., 1992]. Annual inorganic N loading in wet deposition is about twice that of most mountainous areas in the Pacific states and is similar to some areas in the Northeast [Williams et al., 1996].

[11] The Loch Vale watershed is located along the continental divide in Rocky Mountain National Park and ranges in elevation from 3100 to 4000 m. A spruce-fir forest and small subalpine meadows dominate the landscape at the lower elevations. The upper watershed includes large areas of exposed bedrock and talus and some alpine tundra and permanent snowfields.

[12] Selected physical and chemical characteristics of The Loch and Andrews Creek and their associated watersheds are presented in Table 1. Approximately 55 ha (8%) of the Loch Vale watershed is covered by soils (forests, wetlands, and subalpine meadows). The Loch occupies about 5 ha. The remainder of the watershed is exposed bedrock, talus, rocky debris, glaciers and other waters collectively referred to here as “nonvegetated” areas. The 184 ha Andrews Creek subwatershed only includes 18 ha of soil-covered area.

[13] Lake water ANC is defined for use in MAGIC as the charge balance or calculated alkalinity (Calk):

$$\text{Calk} = \text{SBC} - \text{SAA},$$

where SBC is the sum of base cation concentrations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup>) and SAA is the sum of acid anion concentrations (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>), all concentrations in  $\mu\text{eq L}^{-1}$ . The volume-weighted annual average of calculated ANC is 53  $\mu\text{eq L}^{-1}$  for The Loch and 33  $\mu\text{eq L}^{-1}$  for Andrews Creek. Gran titrated ANC values tend to be lower by about 5 to 15  $\mu\text{eq L}^{-1}$  in The Loch, probably due to the influence of organic acids on the titration results. Dissolved organic carbon (DOC) averages about 2 mg L<sup>-1</sup>, but increases to 4 mg L<sup>-1</sup> or higher during early snowmelt. Sulfate

concentrations are relatively high ( $\sim 31 \mu\text{eq L}^{-1}$ ), due partly to watershed sources of  $\text{SO}_4^{2-}$  [Baron *et al.*, 1995]. Nitrate concentrations are moderate ( $\sim 16 \mu\text{eq L}^{-1}$ ). The Loch is also subject to episodic ANC depressions during snowmelt due to dilution of weathering products and a pulse of DOC and  $\text{NO}_3^-$  from soils [Denning *et al.*, 1991].

[14] The hydrologic cycle of Loch Vale is characterized by a lengthy period of snowpack accumulation during autumn, winter, and early spring, followed by a snowmelt period during late spring and early summer. In late summer and early fall, runoff is predominantly base flow, with some snowmelt continuing and some storm flow from precipitation events [Campbell *et al.*, 1995].

[15] Loch Vale watershed exhibits a range of characteristics that contribute to its sensitivity to potential acid deposition impacts, including small size, high elevation, bedrock resistant to weathering, poor soil development, steep slopes, low watershed to lake surface area ratio, short hydraulic retention, high snow accumulation, and short growing season [Baron, 1992]. On the basis of chemistry, The Loch would be classified as moderately sensitive and Andrews Creek as somewhat more sensitive to acidification. Lakes having ANC in the range of 20 to  $50 \mu\text{eq L}^{-1}$  are common in and around Rocky Mountain National Park and lakes having  $\text{ANC} \leq 20 \mu\text{eq L}^{-1}$  are common elsewhere in the Colorado Rocky Mountains [Musselman *et al.*, 1996; Baron *et al.*, 2000]. Nitrate concentrations in many lakes exceed  $10 \mu\text{eq L}^{-1}$ , and in the nearby Green Lakes Valley are increasing over time and are contributing to episodic acidification to ANC values below zero [Williams and Tonnessen, 2000].

[16] The predominant direction of air mass movement over the Front Range is from west to east [Barry, 1973], with periodic upslope movement from the east and southeast [Kelley and Stedman, 1980]. Air masses that move from the southeast toward the park have the potential to transport high levels of nitrogen, sulfur, and ozone-forming compounds to The Loch [Peterson and Sullivan, 1998]. The easterly upslope storm track also carries air masses across agricultural and industrial areas of Colorado before reaching the vicinity of the park [Bowman, 1992]. Higher atmospheric concentration of  $\text{NH}_3$ ,  $\text{NO}_x$ , and nitric acid have been measured near the park during upslope events [Parrish *et al.*, 1986; Langford and Fehsenfeld, 1992].

[17] Baron and Campbell [1997] developed an annual N budget for Loch Vale watershed, based on measured, calculated, and model-simulated values for N inputs, outputs, and internal cycling. They used 9 year average wet deposition values of  $\text{NO}_3^-$ -N ( $1.6 \text{ kg ha}^{-1}$ ) and  $\text{NH}_4^+$ -N ( $1.0 \text{ kg ha}^{-1}$ ) and an assumed ratio of dry to wet N deposition equal to 0.5 to estimate total average N deposition equal to  $3.9 \text{ kg ha}^{-1}$ . An estimated  $1.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  is lost from the watershed via stream flow. Baron and Campbell [1997] concluded that the budget calculations suggested that N storage within bedrock and talus areas was significant, accounting for about 10% of total annual N inputs, and that algal N uptake is important to the overall watershed N budget, despite large N fluxes during spring and summer growing seasons.

[18] Soils of the Loch Vale watershed are similar to other high-elevation soils of the southern Rocky Mountains. They

are coarse-textured, acidic, and often high in coarse fragments [Walshall, 1985]. Soils of the valley slopes and floor developed after retreat of the glaciers. Soil parent material in the cirque valleys above tree line include Neoglacial tills and talus. The broad alpine ridge soils in the upper watershed are much older, having been exposed, unglaciated, since the Cretaceous era [Baron, 1992]. However, soil development on the ridge top is minimal because of the cold, arid environment. Sheer cliffs and steep slopes of talus, scree, and snow separate the ridge from the valley floor by 300–600 m. Conditions are much more favorable for soil development in the lower watershed. Inceptisols and Entisols occur where talus slopes merge into moraine deposits on the valley floor. These grade into Cryoboralfs where the forest is well developed. Organic and alluvial soils are found in areas of low relief and poor drainage adjacent to the stream channels [Baron, 1992]. Alpine soils are classified as Cryorthent and Cryochrept.

## 2.2. Modeling Approach

### 2.2.1. Model Description

[19] MAGIC is a lumped parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry [Cosby *et al.*, 1985a, 1985b]. The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving  $\text{SO}_4^{2-}$  adsorption, cation exchange, dissolution-precipitation- speciation of Al and dissolution-speciation of inorganic C and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

[20] Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and Al. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of  $\text{Al}(\text{OH})_3$ . Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with  $\text{SO}_4^{2-}$  and  $\text{F}^-$ . Effects of  $\text{CO}_2$  on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as triprotic analogues. First-order rates are used for biological retention (uptake) of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the soils and lake. Weathering rates are assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry. For complete details of the model see Cosby *et al.* [1985a, 1985b, 1985c, 1989, 2001].



[21] MAGIC has been used to reconstruct the history of acidification and to simulate the future trends on a regional basis and in a large number of individual catchments in both North America and Europe [e.g., *Lepisto et al.*, 1988; *Whitehead et al.*, 1988; *Cosby et al.*, 1989, 1990, 1996; *Hornberger et al.*, 1989; *Jenkins et al.*, 1990a, 1990b, 1990c; *Wright et al.*, 1990, 1994; *Norton et al.*, 1992; *Sullivan and Cosby*, 1998; *Sullivan et al.*, 2004].

### 2.2.2. Model Implementation

[22] Atmospheric deposition of base cations and strong acid anions are required as inputs to MAGIC. Atmospheric fluxes are calculated from ion concentrations in precipitation and rain and snow amounts, corrected for dry deposition of gas, particulates and aerosols. The model is implemented using average hydrologic and meteorological conditions in a seasonal simulation, driven by mean monthly deposition, precipitation and lake discharge. The exchangeable cation pool in the reference year is estimated from observed soil chemistry and estimated amount of soil.

[23] As implemented here, the model is a three-compartment representation of a catchment. Two compartments are used to represent the terrestrial components of the catchment (nonvegetated areas and soil-covered areas). The third compartment is the lake. Biological uptakes, weathering inputs and equilibrium equations (including soil ion exchange) are used to calculate soil water chemistry. There are no biological uptakes or ion exchange reactions in the nonvegetated compartment, although for simplicity all incoming  $\text{NH}_4^+$  is nitrified before leaching to the lake. The cation output fluxes are estimated from observations of surface water cation concentrations and discharge. Weathering inputs are added to the total deposition, and aqueous phase equilibrium reactions are used to calculate nonvegetated drainage water chemistry. The waters flowing from both soils and nonvegetated areas are then routed to the lake compartment where biological uptake occurs and aqueous phase equilibrium equations are applied to calculate lake water chemistry. The output from MAGIC is a time trace for all major chemical constituents for the period of time chosen for the simulation. Details of the numerical integration and a computer code for implementing the model are given by *Cosby et al.* [1984, 1985a, 1985b, 2001].

[24] The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of fixed parameters within the model that can be directly measured or observed in the system of interest. The weathering and selectivity coefficient of each cation, which determine how tightly the exchangeable cations in the pool are held on the soil matrix, are estimated during the calibration procedure. There are eight unknowns to be optimized (the weathering and the selectivity coefficient of each of the four base cations), and there are eight observations that are used to drive the estimate (current pool size and current output flux of each of the four base cations). The optimization problem is nonlinear and cannot be solved explicitly. Instead, repeated simulations are run, adjusting the eight parameters being optimized after each simulation to produce a smaller weighted sum of squared errors between the eight simulated and observed model outputs.

[25] The model is run using observed and/or assumed atmospheric and hydrologic inputs, and the outputs (lake

water and soil chemical variables, called “criterion” variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called “optimized” parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated.

[26] Estimates of fixed parameters and deposition inputs are subject to uncertainties, so a “fuzzy optimization” procedure was implemented for calibrating the model. It consisted of multiple calibrations using random values of the fixed parameters drawn from the observed possible range of values, and random values of deposition from a range including uncertainty about the estimated values. Each of the multiple calibrations began with (1) a random selection of values of fixed parameters and deposition and (2) a random selection of the starting values of the optimized parameters. The effect on model simulation of uncertainty in the flux measurements is taken into account by calibrating the model multiple times, drawing the target (observed) cation pool and cation fluxes from ranges of possible values around each estimated value. In this application, the range of uncertainty was taken as approximately  $\pm 15\%$  of the observed value for each cation pool or flux. For simulation of future responses at the site, each successful calibration of the model is run, and a range of simulated future responses is derived which incorporates the uncertainty in model inputs. Uncertainty in other inputs and parameters are treated in a similar manner to those for base cations, so that the final calibrations of the model represent the combined uncertainties due to many factors. The optimized parameters were adjusted using the *Rosenbrock* [1960] algorithm to achieve a minimum error fit to the target variables. The final calibrated model was represented by the ensemble of parameter and variable values of 10 separate calibrations.

### 2.2.3. Model Inputs

[27] MAGIC was calibrated to The Loch and to its alpine tributary, Andrews Creek. For the purposes of the model, any nonvegetated areas that drain into an area covered by soil before entering the lake were considered part of the soil compartment (water draining this bare rock is subject to chemical modification by soils in the catchment). Nonvegetated areas that drain directly to the lake were considered part of the modeled nonvegetated compartment. The fact that the model soil compartment consisted of both soil and bare rock areas means that the soil depth used in the model must be an “effective” soil depth (e.g., the depth of soil that would result if the soil present in the catchment were evenly distributed over the soil-covered areas and the nonvegetated areas draining into soil).

[28] Wet deposition was estimated from the NADP/NTN wet deposition monitoring site located at Loch Vale. Monthly median concentrations ( $\mu\text{eq L}^{-1}$ ) of ions in precipitation were used to compute deposition for the years 1992–1996 (Table 2). The average annual precipitation amount (117 cm) and chemistry data were used to calculate fluxes of wet deposition for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ .

[29] Dry deposition of S to the forest in the lower portion of the watershed was estimated to be near zero

**Table 2.** Monthly Average Concentration of Major Ions in Precipitation at Loch Vale During the Period 1992–1996

Month	NADP Concentration, $\mu\text{eq L}^{-1}$								ppt, cm
	Ca	Mg	Na	K	$\text{NH}_4$	$\text{NO}_3$	Cl	$\text{SO}_4$	
1	2.1	0.5	2.5	0.3	3.2	8.6	2.2	7.5	10.9
2	1.9	0.4	1.5	0.1	3.9	6.3	1.0	5.2	10.3
3	3.0	0.6	2.0	0.3	8.2	11.7	1.6	9.5	12.1
4	8.5	2.0	2.2	0.4	7.9	10.4	1.3	10.7	14.9
5	7.7	1.9	2.1	0.4	11.9	14.6	2.0	16.2	10.0
6	10.0	2.5	2.9	1.1	11.8	13.7	2.5	13.8	5.8
7	6.8	1.6	3.1	1.5	11.0	14.0	2.9	16.3	6.0
8	7.4	1.6	3.2	1.0	12.3	17.4	2.9	16.7	5.4
9	7.5	1.7	2.8	0.6	9.4	16.3	2.5	17.3	11.1
10	3.5	0.6	1.5	0.5	5.0	9.0	1.3	9.5	8.4
11	2.5	0.4	1.4	0.2	4.2	9.5	0.9	6.0	9.8
12	4.4	0.9	2.0	0.2	1.6	15.3	2.1	5.2	12.6
Volume weight annual average	5.2	1.2	2.2	0.4	7.0	11.9	1.8	10.5	117.3

by Arthur and Fahey [1993]. Similarly, Campbell *et al.* [1995] found volume-weighted mean  $\text{SO}_4^{2-}$  concentration in the snowpack at maximum accumulation in the Loch Vale watershed similar to volume-weighted mean concentrations in precipitation at the Loch Vale NADP site. This finding suggested that dry deposition of S to the snowpack was negligible. Increased  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations in runoff from bedrock surfaces containing sparse lichen coverage, as compared with  $\text{NO}_3^-$  concentrations in bulk precipitation, suggested that dry deposition could be important during the snow-free season [Clow and Mast, 1995]. Baron and Campbell [1997] estimated dry deposition of N at Loch Vale equal to 50% of measured wet deposition. For the MAGIC model calibration, we assumed that dry deposition of all major ions except  $\text{SO}_4^{2-}$  was equal to 50% of wet deposition inputs. For  $\text{SO}_4^{2-}$ , we assumed that dry deposition equaled 10% of wet deposition.

[30] Discharge at the inflow and outflow of The Loch follows an annual pattern of little or no discharge during winter months, typically November–April, followed by snowmelt, which generally begins in May. Peak discharge is reached in June or early July. Two characteristics of annual snowpack dynamics must be specified for the seasonal application of MAGIC at a site where a snowpack occurs: (1) the months during which snow accumulates and (2) the percentage of ions in the snowpack that is released during each month of the snowmelt.

[31] For every month during the snow accumulation period, the total deposition of each ion was added to the snowpack total for that ion. The effective deposition inputs to the soil in the model for those months were set to zero. Catchment discharge for the snow accumulation months was set to a small value, near zero. During the snowmelt months (which may overlap with accumulation months), the ionic concentrations in snowmelt were adjusted to account for preferential elution of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  early in the melt period [cf. Johannessen and Henriksen, 1978]. It was assumed that 67% of the  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  ions in the snowpack was released with the first 33% of the meltwater.

[32] The total historical atmospheric S deposition was estimated from records of historical emissions for each state within EPA Region IX. Estimated historical emissions for each year in the historical period were normalized to

emissions in the reference year (the year for which observed data were available). This produced a sequence of scale factors that had a value of 1.0 for the reference year. Using this scaled sequence of emissions, historical deposition was estimated by multiplying the total deposition during the reference year 1996 by the emissions scale factor for any year in the past to obtain deposition during that year.

[33] Soils data derived from Baron [1992] were expressed as areal and depth-weighted averages for the watershed (Table 3). The calibration procedure provided estimated values for total weathering of each base cation, which were partitioned between the soil and talus compartments. Assuming weathering rates per unit area in the soil compartment to be 3 times higher than in the non-soil-covered compartment yielded reasonable estimates of lake water base cation concentrations during calibration. This assumption is generally in agreement with the finding of Clow and Sueker [2000] that three watersheds in the park that primarily comprised non-vegetated terrain (Andrews Creek, Icy Brook, Loch Vale) had stream water sum of base cation concentrations about half as high ( $\bar{x} = 89 \mu\text{eq L}^{-1}$ ) as three watersheds that only included about one third nonvegetated terrain (Boulder Brook, Fall River, Big Thompson River;  $\bar{x} = 176 \mu\text{eq L}^{-1}$ ).

[34] The model requires an estimate of the biological uptake of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in each of the model compartments. The following assumptions were made: (1) uptake of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the soil compartment was set to 100%; (2) uptake of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the talus compartment was set to 0%; (3)  $\text{NH}_4^+$  deposited to the talus was nitrified and leached to the lake as  $\text{NO}_3^-$ ; and (4) uptake of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the lake was adjusted such that the estimated catchment output flux of each ion matched observed output fluxes (i.e., lake uptakes were calibrated to observed data).

[35] The monthly average concentrations of ions in lake water were estimated from existing lake water monitoring data [cf. Denning *et al.*, 1991; Baron, 1992; Campbell *et al.*, 1995]. Months with limited available data were assigned lake chemistry values based in part on data for the adjacent months that had measurements. The monthly lake concentrations used in the model calibration are presented in Table 4.

### 3. Results

#### 3.1. Model Calibration

[36] Model simulations of ANC and major ions during the calibration period were generally within  $2 \mu\text{eq L}^{-1}$  of

**Table 3.** Soil Parameters Used in the Model of Acidification of Groundwater in Catchments (MAGIC) Calibration for Loch Vale

Variable	The Loch	Andrews Creek
Average soil depth (where it occurs), m	0.5	0.5
Soil porosity, fraction	0.5	0.5
Lake residence time, years	0.011	0.007
CEC, meq/100 g	31.41	7.39
$E_{\text{Ca}}$ , meq/100 g	4.33	1.04
$E_{\text{Mg}}$ , meq/100 g	1.5	0.16
$E_{\text{Na}}$ , meq/100 g	1.17	0.03
$E_{\text{K}}$ , meq/100 g	1.32	0.09
Soil N content, % (wt/wt)	1.3	0.79
Base saturation, %	26	18
Bulk density, $\text{kg/m}^3$	1005	1005
pH, s.u.	5.2	4.4

**Table 4.** Major Ion Chemistry of The Loch and Andrews Creek Used for Model Calibration, Reported as Median Value of Monthly Samples Collected Between 1992 and 1996<sup>a</sup>

Month	Ca	Mg	Na	K	NH <sub>4</sub>	NO <sub>3</sub>	Cl	SO <sub>4</sub>	ANC <sup>b</sup>	Runoff, cm
<i>The Loch</i>										
1	116.8	30.7	47.9	6.0	1.5	18.8	5.4	62.5	116.2	0
2	108.3	30.1	48.6	5.5	2.3	13.7	5.0	53.8	122.3	0
3	112.3	28.7	46.1	5.8	1.4	11.6	4.7	47.0	130.9	0
4	101.8	27.4	42.2	6.0	1.6	10.7	5.1	43.7	119.5	1
5	75.3	22.7	24.3	5.4	0.9	16.6	5.2	39.6	67.3	11
6	64.1	18.1	20.0	4.2	0.4	20.3	3.5	34.0	49.1	24
7	52.5	12.6	16.9	3.0	0.6	13.0	2.3	24.2	46.0	22
8	46.2	12.3	15.1	2.9	0.0	9.5	2.1	22.7	42.2	13
9	69.2	17.2	21.8	3.9	0.4	17.9	4.0	33.6	57.0	7
10	75.7	21.1	26.5	4.6	0.8	19.9	4.6	38.9	65.3	3
11	92.0	24.2	32.9	4.6	1.1	24.8	4.7	46.2	79.1	1
12	110.3	30.6	40.4	5.5	1.7	24.4	5.2	56.5	102.4	0
Volume weight annual average	62.1	16.8	20.2	3.9	0.5	15.9	3.3	31.1	53.1	84
<i>Andrews Creek</i>										
1										1
2										0
3										0
4	78.9	21.3	25.4	6.7	1.1	28.6	5.3	45.6	54.0	0
5	78.8	20.1	21.4	5.1	1.2	36.6	5.0	41.6	43.3	5
6	60.4	15.0	17.0	3.9	0.7	28.3	3.5	29.9	35.3	28
7	45.9	11.1	14.3	3.0	1.0	18.5	2.6	22.6	31.6	30
8	41.4	10.1	13.9	2.7	0.9	14.6	1.9	21.4	31.1	19
9	54.0	13.4	18.2	3.6	1.1	21.4	2.7	28.6	37.6	10
10	61.2	14.7	21.1	3.6	0.6	24.7	3.1	33.2	40.3	4
11	68.1	16.5	22.3	4.5	1.9	24.7	2.6	34.6	51.5	2
12										1
Volume weight annual average	51.6	12.7	15.8	3.3	0.9	21.6	2.8	26.2	33.7	100

<sup>a</sup>Major ion chemistry in  $\mu\text{eq L}^{-1}$ .<sup>b</sup>ANC is reported as calculated alkalinity (Calk). Gran titrated ANC in The Loch averages about  $17 \mu\text{eq L}^{-1}$  lower than Calk [Baron, 1992].

measured values (Table 5). The results described here were obtained using the average parameter set derived from the 10 calibrations included in the “fuzzy optimization” procedure. The ranges of possible future responses, representing the uncertainty intervals associated with the simulation of each variable, are given in Table 5. Additional

discussion of model uncertainty was provided by Sullivan *et al.* [2004].

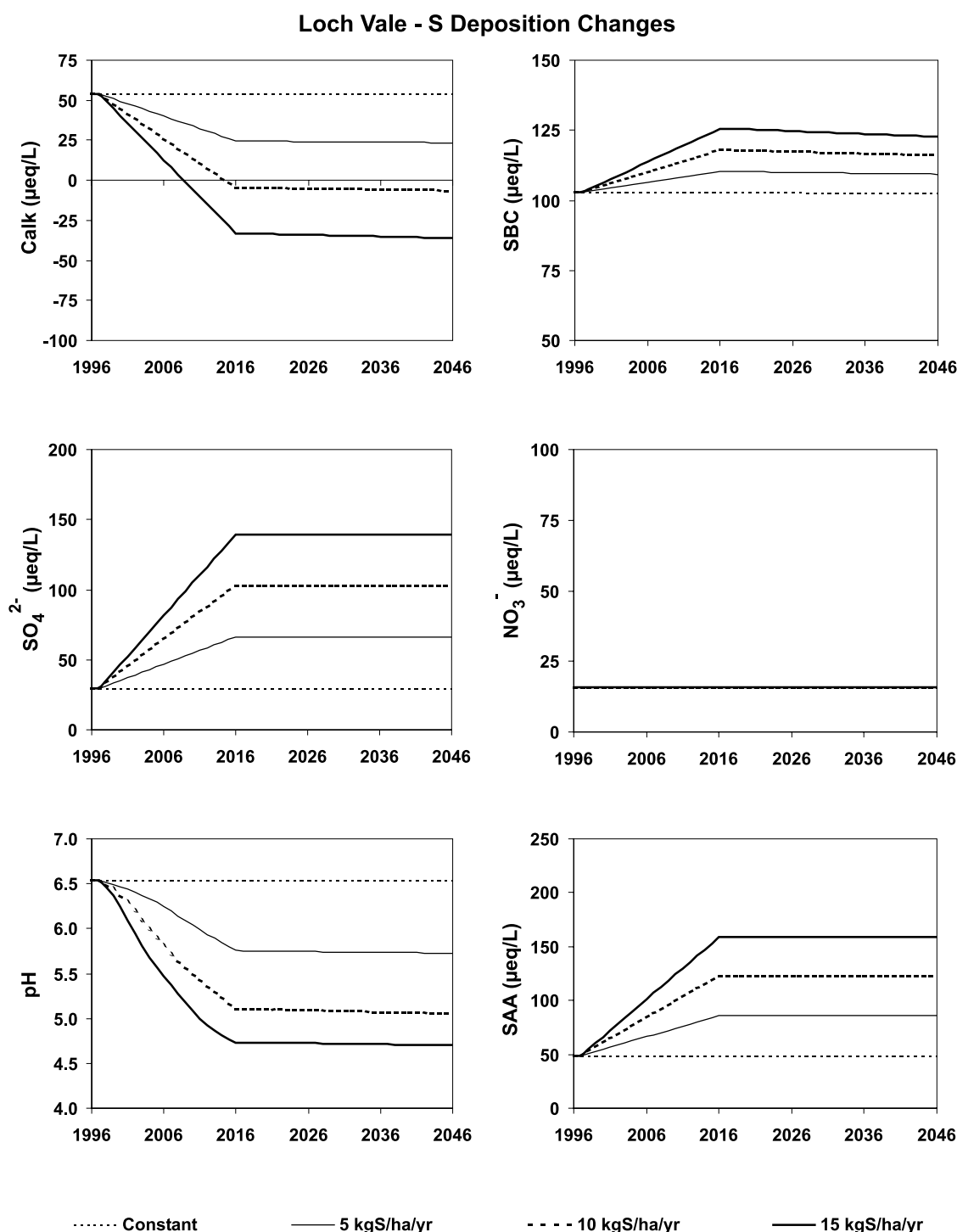
### 3.2. Forecast Scenarios

[37] Four scenarios of future acidic deposition were considered in this study for evaluating acidification relation-

**Table 5.** Calibration Results: Comparison of Simulated and Observed Annual Average Concentrations at The Loch and Andrews Creek for the Calibration Period (1992–1996)<sup>a</sup>

Constituent	The Loch			Andrews Creek		
	Simulated Value	Simulated Range ( $\pm$ )	Observed Value	Simulated Value	Simulated Range ( $\pm$ )	Observed Value
<i>Lake Water Chemistry</i>						
Ca, $\mu\text{eq L}^{-1}$	62	1	62	52	1	52
Mg, $\mu\text{eq L}^{-1}$	17	1	17	13	1	13
Na, $\mu\text{eq L}^{-1}$	20	1	20	16	1	16
K, $\mu\text{eq L}^{-1}$	4	1	4	3	1	3
NH <sub>4</sub> , $\mu\text{eq L}^{-1}$	0		1	0		1
SO <sub>4</sub> , $\mu\text{eq L}^{-1}$	29	3	31	25	4	26
Cl, $\mu\text{eq L}^{-1}$	4	0.3	3	3	0.4	3
NO <sub>3</sub> , $\mu\text{eq L}^{-1}$	16	2	16	21	3	22
SBC, $\mu\text{eq L}^{-1}$	103	2	103	84	3	84
SAA, $\mu\text{eq L}^{-1}$	49	4	50	50	4	51
Calk, $\mu\text{eq L}^{-1}$	54	4	53	34	4	34
pH, s.u.	6.5	0.3	6.5	6.3	0.3	6.6
<i>Soil Chemistry</i>						
Exchangeable Ca, %	13.9	0.2	13.8	14.1	0.1	14.1
Exchangeable Mg, %	4.8	0.2	4.8	2.1	0.1	2.1
Exchangeable Na, %	3.7	0.2	3.7	0.5	0.1	0.5
Exchangeable K, %	4.2	0.2	4.2	1.2	0.1	1.2
Base saturation, %	26.5	0.3	26.5	17.8	0.2	17.8
pH, s.u.	5.2	0.1	5.2	4.5	0.1	4.4

<sup>a</sup>The range indicated for simulated values represents the uncertainty interval derived from the fuzzy optimization procedure, as described in the text.

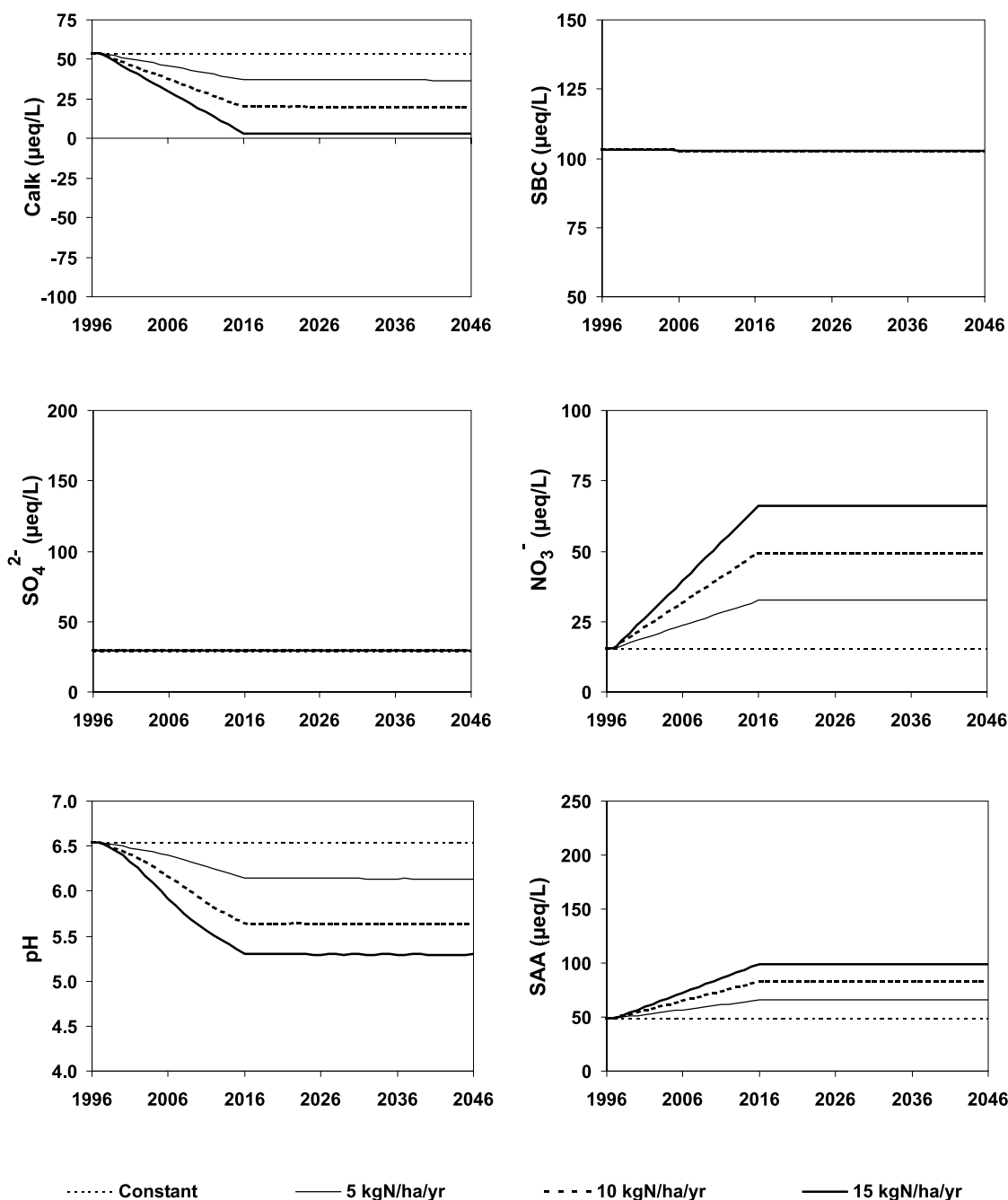


**Figure 1.** Results of future forecast scenarios for changing S deposition at The Loch. Deposition of S was held constant and increased above 1996 values by 5, 10, and 15 kg S ha<sup>-1</sup> yr<sup>-1</sup>.

ships and critical loads: constant deposition at 1996 levels (2.2 kg S ha<sup>-1</sup> yr<sup>-1</sup>, 4.2 kg N ha<sup>-1</sup> yr<sup>-1</sup>) and three levels of increased deposition from 1996 levels. The scenarios were constructed three different ways: (1) only changing S deposition; (2) only changing N deposition; and (3) changing both S and N deposition by equal amounts. All other ions in deposition for each catchment were assumed to remain constant into the future at 1996 levels. Because of the way that the N component of the model is formulated for high-elevation western watersheds, it was not necessary

to apportion the increased N between NO<sub>3</sub>-N and NH<sub>4</sub>-N. The results of the model simulation would be the same. For each scenario, simulations were run for 50 years into the future (1996–2046). For the scenarios assuming increased deposition, the deposition increases were implemented linearly over 20 years (1996–2016), with constant deposition at the higher level assumed for the final 30 years of simulation (2016–2046). The responses of the modeled catchments to the future scenarios are presented in Figures 1–3.

## Loch Vale - N Deposition Changes



**Figure 2.** Results of future forecast scenarios for changing N deposition at The Loch. Deposition of N was held constant and increased above 1996 values by 5, 10, and 15 kg N ha<sup>-1</sup> yr<sup>-1</sup>.

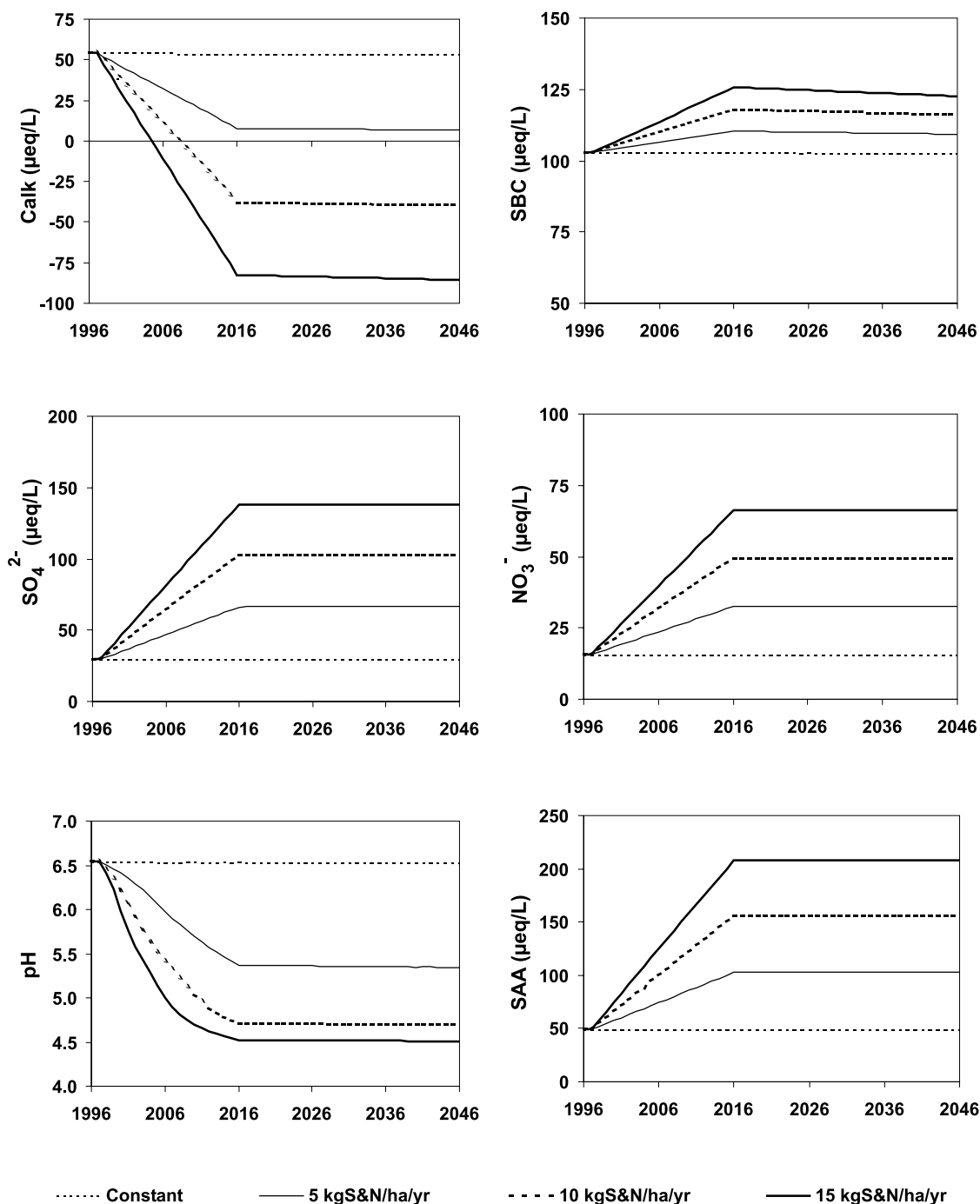
[38] The chemistry of The Loch was projected to change substantially from 1996 values in response to changing S deposition (Figure 1). However, because the initial ANC was relatively high (53 µeq L<sup>-1</sup>), the lake was not projected to become chronically acidic (ANC ≤ 0) even under deposition levels more than double current deposition. An increase in S deposition of 10 kg S ha<sup>-1</sup> yr<sup>-1</sup> was projected to cause lake water SO<sub>4</sub><sup>2-</sup> concentration to increase from 31 to 105 µeq L<sup>-1</sup>, but only to reduce chronic ANC to -6 µeq L<sup>-1</sup>.

[39] As expected, simulated changes in N deposition yielded estimates of projected acidification that were smaller than simulated changes in S deposition (Figure 2). Annual average ANC was projected to decrease from 53 to 6 µeq L<sup>-1</sup> under the scenario of 15 kg N ha<sup>-1</sup> yr<sup>-1</sup> higher than current N deposition. This was because soils are expected to continue to take up some of the increased N inputs, whereas SO<sub>4</sub><sup>2-</sup> is expected to behave conservatively.

[40] The largest amount of chronic acidification was projected to occur if both S and N deposition were to



## Loch Vale - S&amp;N Deposition Changes



**Figure 3.** Results of future forecast scenarios for changing S plus N deposition at The Loch. Deposition was held constant and increased above 1996 values by 5, 10, and 15 kg ha<sup>-1</sup> yr<sup>-1</sup> of both S and N.

increase. A deposition increase by 5 kg ha<sup>-1</sup> yr<sup>-1</sup> for both S and N deposition yielded lake water ANC of 7 µeq L<sup>-1</sup>, in response to lake water concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> equal to 68 and 34 µeq L<sup>-1</sup>, respectively (Figure 3).

### 3.3. Critical Loads Estimates

[41] The estimated critical load of S deposition required to maintain positive chronic ANC in The Loch over a period of 50 years was 11 kg S ha<sup>-1</sup> yr<sup>-1</sup> (Table 6). Model results suggested that the S load would have to be

about 8 kg ha<sup>-1</sup> yr<sup>-1</sup> and 3 kg ha<sup>-1</sup> yr<sup>-1</sup> to maintain ANC above 20 and 50 µeq L<sup>-1</sup>, respectively. Critical loads for N deposition to protect against chronic acidification of The Loch below 0, 20, and 50 µeq L<sup>-1</sup> were higher than those for S: 21, 15, and 6 kg N ha<sup>-1</sup> yr<sup>-1</sup>, respectively.

[42] Modeling results for Andrews Creek suggested that substantially lower levels of S and/or N deposition would be required in order to protect against chronic acidification. For example, S deposition equal to 8.1 and 4.6 kg ha<sup>-1</sup> yr<sup>-1</sup> would be required to protect against acidification of

**Table 6.** Simulated Critical Load of S or N Required to Reduce the ANC of The Loch and Andrews Creek to 0, 20, or 50  $\mu\text{eq L}^{-1}$  by the Year 2046<sup>a</sup>

Deposition	ANC Limit = 0		ANC Limit = 20 $\mu\text{eq L}^{-1}$		ANC Limit = 50 $\mu\text{eq L}^{-1}$	
	The Loch	Andrews Creek	The Loch	Andrews Creek	The Loch	Andrews Creek
Nitrogen	20.6	12.2	14.7	7.8	5.8	NR <sup>b</sup>
Sulfur	11.1	8.1	7.8	4.6	2.8	NR <sup>b</sup>

<sup>a</sup>Critical load in  $\text{kg ha}^{-1} \text{yr}^{-1}$  of S or N.<sup>b</sup>Ecological endpoint (ANC = 50  $\mu\text{eq L}^{-1}$ ) could not be achieved (no recovery) by 2046 even if deposition of N or S was reduced to zero.

Andrews Creek within 50 years to ANC = 0 and 20  $\mu\text{eq L}^{-1}$ , respectively. These lower simulated values of critical S load were mostly attributable to the lower current ANC of this tributary stream (33  $\mu\text{eq L}^{-1}$ ). Similarly, Andrews Creek critical load estimates for N were about two thirds of those for The Loch, in part because of the lower baseline ANC and in part because  $\text{NO}_3^-$  concentrations were higher (21 versus 16  $\mu\text{eq L}^{-1}$ ), suggesting lower watershed retention of atmospherically deposited N.

## 4. Discussion

### 4.1. Model Assumptions

[43] MAGIC, like any process model, includes many limitations and uncertainties, although it has been extensively tested [cf. *Sullivan and Cosby*, 1995, 1998; *Sullivan et al.*, 1996; *Cosby et al.*, 1995, 1996, 2001]. Chief among these uncertainties for high-elevation western watersheds is the role of talus in acid neutralization and N retention, and the extent to which N saturation of alpine soils can be predicted from empirical data.

[44] In undisturbed alpine and subalpine terrestrial ecosystems, the limiting factor for primary production is often N supply, which is largely determined by the ability of soil microbes to fix atmospheric  $\text{N}_2$  and to mineralize organic N. Most terrestrial ecosystems are considered N-limited [*Friedland et al.*, 1991; *Bowman et al.*, 1993]. Inputs of anthropogenic atmospheric N to alpine plant communities have the potential to alter plant community structure and increase sensitivity to water stress, frost and herbivory [*Bowman et al.*, 1993], as well as to contribute  $\text{NO}_3^-$  to drainage waters.

[45] *Rueth et al.* [2003] reported results of N fertilization on Loch Vale soils. Nitrate leaching of N occurred in response to very large additions (25  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) of N for a 3 year period. Furthermore, empirical studies in Europe have suggested that N deposition must be considerably higher than currently occurs at Loch Vale before soils become N saturated and begin to leach  $\text{NO}_3^-$  to surface waters. *Dise and Wright* [1995] examined watershed and plot-scale input-output budgets for N across Europe and found elevated N leaching at sites that received in excess of about 10  $\text{kg ha}^{-1} \text{yr}^{-1}$  of N, about two and a half times the deposition received by the Loch Vale watershed. *Sullivan et al.* [1997] found that the observed fall  $\text{NO}_3^-$  concentration in Adirondack Mountain lakes, New York, could largely be explained by  $\text{NO}_3^-$  deposition directly to the lake surface without the need for  $\text{NO}_3^-$  leaching from watershed soils. Those lakes that did show lake water  $\text{NO}_3^-$  concentrations higher than would be predicted from direct  $\text{NO}_3^-$  deposition to the lake surface were generally among the most acid sensitive of the study lakes (pH 4.7 to 5.3) and received

generally high levels of N deposition ( $\sim 10\text{--}12 \text{ kg N ha}^{-1} \text{yr}^{-1}$ ) [*Ollinger et al.*, 1993]. Thus the assumption that watershed soils at Loch Vale take up 100% of incoming N seems reasonably robust under current and moderately increased N deposition.

[46] It appears that much of the N deposited on talus and bedrock areas is transported to surface waters with little assimilation. Nevertheless, it is clear that talus and exposed bedrock surfaces are not inert, although few studies have been conducted to examine changes in runoff chemistry attributable to chemical and biological reactions in these important watershed compartments. *Baron and Campbell* [1997] inferred that rock outcrops and talus in the Loch Vale watershed were biologically active and influenced stream chemistry. Mass balance calculations suggested that about 10% of atmospheric N inputs may be immobilized or stored in the bedrock compartment of the watershed. *Clayton* [1998] showed increased ANC of snowmelt and rain after 15–50 m transport over rock, lichens, and thin pockets of saprolite and soil in the Wind River Mountains, Wyoming. Similar findings were reported by *Eilers and Vaché* [1998] in Goat Rocks Wilderness, Washington. In a modeling sensitivity study of Andrews Creek using the Alpine Hydrochemical Model, *Meixner et al.* [2000] found that nearly all  $\text{NH}_4^+$  deposited in the watershed was assimilated or nitrified.

[47] Calibration of watershed N outputs under these assumptions, and consequent model estimates of lake water  $\text{NO}_3^-$  concentrations in The Loch, yielded plausible results. Only 5% of in-lake  $\text{NO}_3^-$  had to be taken up by aquatic organisms to result in an input-output N balance for the catchment as a whole. Further research is required to refine our understanding of the net effect of alpine watershed processes on N leaching, especially from exposed rock surfaces. It is clear that such processes are spatially variable. For example, *Campbell et al.* [2000] found that N outputs from the Andrews Creek subwatershed of Loch Vale approximately equaled inputs, whereas N retention was much greater in the Icy Brook subwatershed.

[48] Weathering of talus and poorly developed soil can provide substantial base cation contributions to runoff [*Clow et al.*, 1997], and *Clow and Drever* [1996] concluded that weathering in alpine settings is likely proportional to seasonal precipitation. In many cases, episodic processes may depart substantially from some of the simplifying assumptions used for modeling chronic chemistry. For example, during snowmelt, soil nitrogen can be flushed into drainage waters [cf. *Campbell et al.*, 1995; *Kendall et al.*, 1995]. MAGIC is structured to model long-term chronic water chemistry, however, and episodic processes are not explicitly considered. The likelihood that episodes result in

greater acidity in the short term must be considered when interpreting MAGIC output.

## 4.2. Critical Loads

### 4.2.1. Criteria for Standards

[49] Consideration of acid deposition standards for the protection of surface water quality from potential adverse effects of S and N deposition is a multifaceted problem requiring that S and N be treated separately as potentially acidifying agents. Appropriate criteria must be selected as being indicative of damaged water quality, for example ANC,  $\text{NO}_3^-$  concentration, or pH. Once a criterion has been selected, a critical value must be estimated, above or below which the criterion should not be permitted to rise or fall. Selection of critical values for ANC or pH is confounded by the existence of lakes and streams that are low in pH or ANC due entirely to natural factors, irrespective of acidic deposition. In particular, low concentrations of base cations in solution, due to low weathering rates and/or minimal contact between drainage waters and mineral soils, and high concentrations of organic acids contribute to naturally low pH and ANC in some surface waters.

[50] Acid deposition standards might be selected on the basis of protecting aquatic systems from chronic acidification; conversely, episodic acidification might also be considered, and would be of obvious importance in regions such as the Rocky Mountains where hydrology is dominated by spring snowmelt. Episodic acidification is considered to be biologically relevant for high-elevation aquatic ecosystems in the western United States [e.g., *Barmuta et al.*, 1990; *Kratz et al.*, 1994]. High-elevation aquatic ecosystems such as The Loch are sensitive to fertilization, as well as acidification, effects of N deposition. Thus selection of appropriate acid deposition standards involves consideration of a matrix of factors.

[51] A target load [cf. *Henriksen and Brakke*, 1988] can be based on political, economic, or temporal considerations, and may imply that the environment will be protected to a specified level (i.e., certain degree of allowable damage) and/or over a specified period of time. There has been a rapid acceptance of the concepts of critical and target loads throughout Europe and in Canada for use in political negotiations concerning air pollution and development of abatement strategies to mitigate environmental damage [e.g., *Posch et al.*, 1997].

[52] Criteria of unacceptable change used in critical loads assessments are typically set in relation to known or expected effects on aquatic or terrestrial organisms. For protection of aquatic organisms, the ANC of runoff water is most commonly used [Nilsson and Grennfelt, 1988; *Henriksen and Brakke*, 1988; *Sverdrup et al.*, 1990]. Concentrations below which ANC should not be permitted to fall, have been set at 0, 20, and  $50 \mu\text{eq L}^{-1}$  for various applications [e.g., *Kämäri et al.*, 1992].

### 4.2.2. Estimates for Loch Vale

[53] The estimated F factor (change in sum of base cation concentration divided by change in  $\text{SO}_4^{2-}$  plus  $\text{NO}_3^-$  concentration) [Henriksen, 1982; Sullivan, 1991] for The Loch, based on the scenario of increasing S and N deposition by  $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$  each, was about 0.34. In other words 34% of the change in lake water  $\text{SO}_4^{2-} + \text{NO}_3^-$

concentration was projected to result in a stoichiometric increase in base cation concentrations. The remaining 66% was projected to result in decreased ANC. This lake would be considered sensitive to acidic deposition impacts. However, the current lake water ANC is not excessively low. The estimated load of S required to reduce the ANC of Loch Vale to zero on a chronic basis was  $11 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  (Table 6), about 5 times 1996 deposition. Similarly, the estimated load of N required to reduce the ANC of The Loch to zero was  $21 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (Table 6), about 5 times current N deposition. Somewhat lower levels of deposition would be required to reduce episodic stream or lake water ANC to zero, or to reduce chronic ANC to  $20 \mu\text{eq L}^{-1}$ , probably on the order of 3 to 4 times current deposition (Table 6). ANC equal to  $50 \mu\text{eq L}^{-1}$  was projected to occur if N deposition was increased to  $5.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$  or S deposition to  $2.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ , in each case an increase of less than 40% above reference year values. The results of this modeling exercise suggest that The Loch is moderately well buffered and would not be expected to chronically acidify to ANC below  $20 \mu\text{eq L}^{-1}$  under foreseeable future deposition scenarios. Critical load estimates for the Andrews Creek subwatershed were about two thirds of the values estimated for The Loch. It was estimated that either an S deposition load of  $4.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  or an N deposition load of  $7.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  would cause Andrews Creek to decline to ANC below  $20 \mu\text{eq L}^{-1}$  within 50 years. These estimates compare with 1996 deposition of about  $2.2 \text{ kg S}$  and  $4.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , respectively. The simulation suggested that  $\text{ANC} = 50 \mu\text{eq L}^{-1}$  could not be achieved in Andrews Creek by 2046, even if S or N was reduced to zero (Table 6). The simulated preindustrial ANC of Andrews Creek was only  $62 \mu\text{eq L}^{-1}$ . Therefore it may be necessary to reduce both S and N deposition substantially and/or wait longer than 50 years to achieve the targeted ANC value in this stream.

[54] The Loch is clearly not representative of the most acid-sensitive lakes in the Front Range. For example, *Eilers et al.* [1989] reported that 20% of the wilderness lakes in the Front Range had Gran titrated  $\text{ANC} \leq 41 \mu\text{eq L}^{-1}$  (similar to The Loch) and the median ANC was about  $80 \mu\text{eq L}^{-1}$ , based on data from EPA's Western Lakes Survey [Landers et al., 1987].

[55] MAGIC has been applied to some lakes in the Rocky Mountains that are considerably more acid-sensitive than The Loch. For example, critical loads of S and N were calculated for White Dome Lake, situated at 3850 m elevation in the Weminuche Wilderness, CO [Sullivan et al., 1998]. The 156 ha watershed of White Dome Lake is entirely alpine, about 94% of which is exposed bedrock and talus. The volume-weighted annual average lake water concentrations of both  $\text{NO}_3^-$  ( $6 \mu\text{eq L}^{-1}$ ) and  $\text{SO}_4^{2-}$  ( $31 \mu\text{eq L}^{-1}$ ) are relatively high, and lake water ANC is only  $10 \mu\text{eq L}^{-1}$ . Critical loads estimates suggested that S deposition would only have to increase by about 30% above current values (to  $6.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) or N deposition to increase by  $6.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  to reduce chronic lake water ANC to zero [Sullivan et al., 1998]. Thus the estimated critical load values to protect against  $\text{ANC} \leq 0$ , for the three surface waters in Colorado for which critical loads have been calculated with MAGIC, vary from 6.6 to  $11.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  and vary in proportion to the ANC of the

**Table 7.** Change in Deposition Levels Above 1996 Deposition Amounts at Which the MAGIC Model Simulated an Absolute Change of  $10 \mu\text{eq L}^{-1}$  or a Proportional Change of 10% in the Water Concentration Observed in the Reference Year (1996) of One of the Key Parameters in Loch Vale and Andrews Creek<sup>a</sup>

	ANC		NO <sub>3</sub>	
	The Loch	Andrews Creek	The Loch	Andrews Creek
<i>Increased Sulfur Deposition</i>				
Criterion = $10 \mu\text{eq L}^{-1}$ decrease in ANC	1.6	1.7		
Criterion = 10% decrease in ANC	0.8	0.5		
<i>Increased Nitrogen Deposition</i>				
Criterion = $10 \mu\text{eq L}^{-1}$ decrease in ANC or increase in NO <sub>3</sub> concentration	2.9	2.2	3.0	2.2
Criterion = 10% decrease in ANC or increase in NO <sub>3</sub> concentration	1.5	0.8	0.5	0.5

<sup>a</sup>Deposition levels are in  $\text{kg ha}^{-1} \text{yr}^{-1}$  of S or N. Deposition in 1996 was 2.2 and  $4.6 \text{ kg ha}^{-1} \text{yr}^{-1}$  of S and N, respectively.

water. Issues of scale and representativeness are important, and it would be inadvisable to base environmental policy on modeling results for only a few lakes.

#### 4.3. Alternatives to the Critical Load Modeling Approach

[56] The Rocky Mountain region of the U.S. Forest Service adopted Limits of Acceptable Change (LAC) as a general guideline to define the boundary conditions beyond which impacts would be considered adverse or unacceptable [Haddow *et al.*, 1998]. The LAC guidelines were established at a workshop in 1990 that involved federal land managers, air regulatory agencies, and research scientists. The goal of the workshop was to establish Forest Service procedures for evaluating pollution impacts to wilderness areas within the Rocky Mountain region. For lakes having ANC below  $25 \mu\text{eq L}^{-1}$ , it was implicitly assumed that the LAC had already been exceeded and the recommended allowable change was zero, in order that further degradation would be avoided. In practice, the Forest Service has used an LAC criterion of  $1 \mu\text{eq L}^{-1}$  change in ANC for such ultrasensitive lakes in conjunction with PSD evaluations (D. Haddow, personal communication, 2000).

[57] The LAC approach for the various parameters of interest can also be examined using the MAGIC model output. For example, an LAC can be set at 10% for ANC; in other words, current ANC should not be permitted to decrease by more than 10% of its current value. Thus using the 10% LAC, The Loch would be protected against an ANC decline of  $5 \mu\text{eq L}^{-1}$  (Table 7). An increase in S deposition of about  $0.8 \text{ kg S ha}^{-1} \text{yr}^{-1}$  was projected to deplete the ANC of Loch Vale about  $5 \mu\text{eq L}^{-1}$ . An increase in N deposition of about  $1.5 \text{ kg N ha}^{-1} \text{yr}^{-1}$  was projected to have a comparable effect (Table 7).

[58] Evaluation of LAC on a percentage change basis for lakes that are lower in ANC than Loch Vale is more problematic. For example, for lakes having current ANC below about  $20 \mu\text{eq L}^{-1}$ , evaluation of the change in deposition that would be required to change the ANC by 10% ( $<2 \mu\text{eq L}^{-1}$ ) is rather meaningless from a scientific perspective for reasons related to measurement errors and model resolution. For example, measured ANC of The Loch during any given month varies by at least  $10 \mu\text{eq L}^{-1}$ , and the uncertainty in estimating annual average ANC is on the order of about  $10 \mu\text{eq L}^{-1}$ , based on our experience. Also, model testing at the subalpine experimental research catchment Risdalsheia, in southern Norway, suggested that MAGIC was able to project annual average ANC change

in response to changing deposition over an 8 year period of record with an error of about  $5 \mu\text{eq L}^{-1}$  [Cosby *et al.*, 1995]. It may therefore be useful to evaluate the LAC for some lakes using a criterion of acceptable change equal to either 5 or  $10 \mu\text{eq L}^{-1}$ , rather than 10% of the current value. This issue can also be examined for other potentially important values besides ANC, for example for NO<sub>3</sub><sup>-</sup> which can alter biological communities due to its fertilizing influence.

[59] MAGIC was used to estimate the change in S or N deposition that would be required to change the ANC and NO<sub>3</sub><sup>-</sup> concentrations in The Loch and Andrews Creek by  $10 \mu\text{eq L}^{-1}$  (Table 7). Simulated increases in S deposition of 1.6 and  $1.7 \text{ kg ha}^{-1} \text{yr}^{-1}$  were projected to reduce lake water ANC by  $10 \mu\text{eq L}^{-1}$  in The Loch and Andrews Creek, respectively. Similarly, simulated increases in N deposition of 3.0 and  $2.2 \text{ kg ha}^{-1} \text{yr}^{-1}$  were projected to increase lake water NO<sub>3</sub><sup>-</sup> concentration by  $10 \mu\text{eq L}^{-1}$  in these two water bodies.

[60] Criteria for resource protection can also be estimated empirically. For example, Williams and Tonnessen [2000] reported episodic acidification to ANC  $< 0$  of two headwater streams in the Green Lakes Valley, Colorado. Elevated NO<sub>3</sub><sup>-</sup> concentrations during snowmelt were associated with negative ANC values in both streams, in response to inorganic N deposition of about  $3.5 \text{ kg ha}^{-1} \text{yr}^{-1}$ . On the basis of these data, and also the results of synoptic lake surveys in the Colorado Front Range, Williams and Tonnessen [2000] recommended establishment of a critical load for wet N deposition to Class I areas in the central Rocky Mountains of  $4 \text{ kg N ha}^{-1} \text{yr}^{-1}$ , which would likely correspond to total N deposition near  $6 \text{ kg N ha}^{-1} \text{yr}^{-1}$ . Such a level is similar to our modeled critical N load for protecting White Dome Lake against chronic acidification to ANC below zero, but is substantially lower than our results for either The Loch or Andrews Creek. The recommended generic critical N load value of Williams and Tonnessen [2000] for the central Rocky Mountains is about 30% lower than the MAGIC model estimate of the critical load to protect Andrews Creek from ANC below  $20 \mu\text{eq L}^{-1}$ . It is not surprising that critical loads should vary across the region. For that reason, it is important to determine the distribution of critical loads that would be needed to protect the range of resources against adverse impacts.

#### 4.4. Selection of Management Criteria

[61] Clearly, the selection of appropriate targets and associated critical loads strongly influence interpretation of the model output for any watershed. The goal of the



PSD process is to protect sensitive resources from adverse impacts. Unfortunately, the lower limit of acid-base chemical change (e.g., in ANC) that would elicit a biological response in high-elevation, oligotrophic western lakes is not known. Various species of fish have been shown to respond to lowered pH by exhibiting higher mortality, particularly at pH levels near 5.0, which roughly correspond with ANC = 0. Experimental depressions in pH and ANC, equivalent to spring snowmelt pulses, have been shown to affect high-elevation stream invertebrate populations [Kratz *et al.*, 1994] and lake zooplankton [Barmuta *et al.*, 1990]. Once these dose-response relationships have been established for sensitive regions of the west, FLMS can use the associated change in surface water chemistry during hydrologic episodes as part of the basis for setting target loads of deposition.

[62] Sensitive fish species in Rocky Mountain National Park include both native and nonnative salmonids. Hybrid greenback cutthroat trout (*Onchorhynchus clarkii stomias*) occur in The Loch. It has been shown that native western trout are sensitive to short-term increases in acidity. For example, Woodward *et al.* [1989] exposed native western cutthroat trout to pH depressions (pH 4.5 to 6.5) in the laboratory. Reductions in pH from 6.5 to 6.0 in low-calcium water ( $70 \mu\text{eq L}^{-1}$ ) did not affect survival, but did reduce growth of swim-up larvae. Eggs, alevins, and swim-up larvae showed significantly higher mortality at pH 4.5 as compared to pH 6.5. Mortality was also somewhat higher at pH 5.0, but only statistically higher for eggs.

[63] Some species of aquatic biota have been shown to be somewhat more sensitive to pH and ANC change than are cutthroat trout [Baker *et al.*, 1990]. A critical load threshold of ANC = 0 can easily be defended as a threshold below which chemical changes are likely to affect native fish populations. ANC thresholds of 20 and  $50 \mu\text{eq L}^{-1}$  provide a margin of error to allow for episodic ANC depressions during snowmelt or rainfall events. Some species of aquatic biota are probably sensitive to ANC change below  $20 \mu\text{eq L}^{-1}$ , although it is less certain that ANC changes at or below  $50 \mu\text{eq L}^{-1}$  result in direct biological effects in high-elevation western systems [e.g., Barmuta *et al.*, 1990].

[64] In the Adirondack Mountains of New York, about half of the 52 fish species recorded in the Adirondack Lakes Survey [Kretser *et al.*, 1989] did not occur in lakes having pH less than 6 [Driscoll *et al.*, 2003]. Such lakes have ANC below about  $30 \mu\text{eq L}^{-1}$  [Munson *et al.*, 1990]. A pH = 6 threshold has been cited as a recovery goal for acidified lakes in eastern Canada [Holt and Yan, 2003] and ANC = 20 for an acidified river in Norway [Raddum and Fjellheim, 2003].

[65] The LAC for The Loch, based on the Forest Service criterion of less than 10% allowable change in ANC [Haddow *et al.*, 1998], would limit deposition increases to no more than  $0.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  or  $1.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ . For Andrews Creek, these allowable deposition increases would be even smaller,  $0.5$  and  $0.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of S and N, respectively (Table 7). Whether or not such small changes in deposition would result in any biological effects from acidification is not known.

[66] It is likely that some biological effects have already occurred, under current deposition, especially to algal communities. For example, diatom assemblages in The

Loch shifted from primarily oligotrophic taxa to a flora that included more mesotrophic species after about 1950 [Baron *et al.*, 2000]. Nitrogen is no longer a limiting nutrient in The Loch, whereas evidence suggests that similar lakes 100 km to the north are strongly N-limited [Lafrancois *et al.*, 2004]. Such effects are probably due more to the fertilizing influence of increased N supply than to the loss of ANC that has occurred to date [Baron *et al.*, 1998].

[67] Selection of the best, or most appropriate, criterion and target load for protecting aquatic resources in Loch Vale is not a scientific issue. It is a policy issue that must be addressed by land managers, based in part on the best available scientific information. FLMS may want to protect the sensitive resource against biological changes that are difficult or impossible to measure or to attribute to atmospheric deposition. Simulations from MAGIC, or other watershed models, can provide useful information to be used in the decision process. However, the final determination must be based on policy judgment, not science.

[68] The results of MAGIC model simulations presented here for The Loch and Andrews Creek provide part of the scientific foundation for management decisions regarding the protection of aquatic resources in this one watershed. Additional steps in the continuing process of evaluating and establishing appropriate deposition levels for resource protection in Class I areas could include acid-base chemistry modeling for a regionally representative selection of watersheds chosen to represent Class I areas of the Front Range or the region as a whole. An assessment of potential changes in aquatic ecosystem structure and function in response to the fertilizing effects of N is also needed. The results of such efforts would allow incorporation of regional variability in acid sensitivity and eutrophication effects into the scientific foundation for the resource protection decision process.

[69] **Acknowledgments.** This research was supported by a grant from the National Park Service, Air Resources Division to the University of Virginia. Helpful suggestions were provided for an earlier draft of this manuscript by J. Baron and D. Campbell.

## References

- Arthur, M. A., and T. J. Fahey (1993), Throughfall chemistry in an Engelmann spruce-subalpine fir forest in north central Colorado, *Can. J. For. Res.*, **23**, 738–742.
- Baker, J. P., D. P. Bernard, S. W. Christensen, and M. J. Sale (1990), Biological effects of changes in surface water acid-base chemistry, *State Sci. Technol. Rep. 13*, Natl. Acid Precip. Assess. Prog., Washington, D. C.
- Barmuta, L. A., S. D. Cooper, S. K. Hamilton, K. W. Kratz, and J. M. Melack (1990), Responses of zooplankton and zoobenthos to experimental acidification in a high elevation lake (Sierra Nevada, California, U.S.A.), *Freshw. Biol.*, **23**, 571–586.
- Baron, J. (1992), *Biogeochemistry of a Subalpine Ecosystem: Loch Vale Watershed*, *Ecol. Stud. Ser.*, vol. 90, Springer-Verlag, New York.
- Baron, J. S., and D. H. Campbell (1997), Nitrogen fluxes in a high elevation Colorado Rocky Mountain basin, *Hydrol. Processes*, **11**, 783–799.
- Baron, J., E. J. Allstott, and B. K. Newkirk (1995), Analysis of long term sulfate and nitrate budgets in a Rocky Mountain basin, *IAHS Publ.*, **228**, 255–261.
- Baron, J. S., J. T. Minear, H. M. Rueth, K. R. Nydick, B. M. Moraska, B. M. Johnson, and E. J. Allstott (1998), Ecosystem responses to nitrogen deposition in the Colorado Front Range (abstract), *Eos Trans. AGU*, **79**(45), Fall Meet. Suppl., F319.
- Baron, J. S., H. M. Rueth, A. M. Wolfe, K. R. Nydick, E. J. Allstott, J. T. Minear, and B. Moraska (2000), Ecosystem responses to nitrogen deposition in the Colorado Front Range, *Ecosystems*, **3**, 352–368.
- Barry, R. G. (1973), A climatological transect of the east slope of the Front Range, Colorado, *Arct. Alp. Res.*, **5**, 89–110.

- Bowman, W. D. (1992), Inputs and storage of nitrogen in winter snowpack in an alpine ecosystem, *Arct. Alp. Res.*, 24, 211–215.
- Bowman, W., T. Theodore, J. Schardt, and R. Conant (1993), Constraints of nutrient availability on primary production in two alpine tundra communities, *Ecology*, 74, 2085–2097.
- Bull, K. R. (1992), An introduction to critical loads, *Environ. Pollut.*, 77, 173–176.
- Bunyak, J. (1993), Permit application guidance for new air pollution sources, *Nat. Resour. Rep. 93-09, Rep. B-79-2*, U.S. Dep. of the Int. Natl. Park Serv., Washington, D. C.
- Campbell, D. H., D. W. Clow, G. P. Ingersoll, M. A. Mast, N. E. Spahr, and J. T. Turk (1995), Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains, *Water Resour. Res.*, 31, 2811–2822.
- Campbell, D. H., J. S. Baron, K. A. Tonnessen, P. D. Brooks, and P. F. Schuster (2000), Controls on nitrogen flux in alpine/subalpine watersheds, *Water Resour. Res.*, 36, 49–62.
- Clayton, J. L. (1998), Alkalinity generation in snowmelt and rain runoff during short distance flow over rock, *Res. Pap. RMRS-RP-12*, U.S. Dep. of Agric. For. Serv. Rocky Mt. Res. Station, Ogden, Utah.
- Clow, D. W., and J. I. Drever (1996), Weathering rates as a function of flow through an alpine soil, *Chem. Geol.*, 132, 131–141.
- Clow, D. W., and M. A. Mast (1995), Composition of precipitation, bulk deposition, and runoff at a granitic bedrock catchment in the Loch Vale Watershed, Colorado, USA, in *Biogeochemistry of Seasonally Snow-Covered Catchments*, edited by K. A. Tonnessen, M. W. Williams, and M. Tranter, pp. 235–242, Int. Assoc. of Hydrol. Sci., Boulder, Colo.
- Clow, D. W., and J. K. Sucker (2000), Relations between basin characteristics and stream water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado, *Water Resour. Res.*, 36, 63–76.
- Clow, D. W., M. A. Mast, T. D. Bullen, and J. T. Turk (1997), Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado, *Water Resour. Res.*, 33, 1335–1351.
- Cosby, B. J., R. F. Wright, G. M. Hornberger, and J. N. Galloway (1984), Model of acidification of groundwater in catchments, project completion report, *Proj. E2-14*, Environ. Protect. Agency N.C. State Univ. Acid Precip. Prog., Raleigh, N. C.
- Cosby, B. J., R. F. Wright, G. M. Hornberger, and J. N. Galloway (1985a), Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry, *Water Resour. Res.*, 21, 51–63.
- Cosby, B. J., R. F. Wright, G. M. Hornberger, and J. N. Galloway (1985b), Modelling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment, *Water Resour. Res.*, 21, 1591–1601.
- Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright (1985c), Time scales of catchment acidification: A quantitative model for estimating freshwater acidification, *Environ. Sci. Technol.*, 19, 1144–1149.
- Cosby, B. J., G. M. Hornberger, P. F. Ryan, and D. M. Wolock (1989), MAGIC/DDRP final report, project completion report, U.S. Environ. Protect. Agency Direct/Delayed Response Proj., Corvallis, Oreg.
- Cosby, B. J., A. Jenkins, J. D. Miller, R. C. Ferrier, and T. A. B. Walker (1990), Modelling stream acidification in afforested catchments: Long-term reconstructions at two sites in central Scotland, *J. Hydrol.*, 120, 143–162.
- Cosby, B. J., R. F. Wright, and E. Gjessing (1995), An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway, *J. Hydrol.*, 170, 101–122.
- Cosby, B. J., S. A. Norton, and J. S. Kahl (1996), Using a paired-watershed manipulation experiment to evaluate a catchment-scale biogeochemical model, *Sci. Tot. Environ.*, 183, 49–66.
- Cosby, B. J., R. C. Ferrier, A. Jenkins, and R. F. Wright (2001), Modelling the effects of acid deposition: Refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model, *Hydrol. Earth Syst. Sci.*, 5, 499–517.
- Denning, A. S., J. Baron, M. A. Mast, and M. Arthur (1991), Hydrologic pathways and chemical composition of runoff during snowmelt in Loch Vale watershed, Rocky Mountain National Park, Colorado, USA, *Water Air Soil Pollut.*, 59, 107–123.
- Dise, N. B., and R. F. Wright (1995), Nitrogen leaching from European forests in relation to nitrogen deposition, *For. Ecol. Manage.*, 71, 153–161.
- Driscoll, C., et al. (2003), Nitrogen pollution in the northeastern United States: Sources, effects and management options, *Bioscience*, 53, 357–374.
- Eilers, J. M., and K. B. Vaché (1998), Lake response to atmospheric and watershed inputs in the Goat Rocks wilderness, WA, final report to Weyerhaeuser Paper Co., E&S Environ. Chem. Inc., Corvallis, Oreg.
- Eilers, J. M., D. F. Brakke, D. H. Landers, and W. S. Overton (1989), Chemistry of lakes in designated wilderness areas in the western United States, *Environ. Monit. Assess.*, 12, 3–21.
- Friedland, A. J., E. K. Miller, J. J. Battles, and J. T. Thorne (1991), Nitrogen deposition, distribution and cycling in a subalpine spruce-fir forest in the Adirondacks, New York, USA, *Biogeochemistry*, 14, 31–55.
- Gundersen, P. (1992), Mass balance approaches for establishing critical loads for nitrogen in terrestrial ecosystems, background document, UN-ECE Workshop Critical Loads for Nitrogen, Løkeberg, Sweden.
- Haddow, D., R. Musselman, T. Blett, and R. Fisher (1998), Guidelines for evaluating air pollution impacts on wilderness within the Rocky Mountain region: Report of a workshop, 1990, *Gen. Tech. Rep. RMRS-GTR-4*, U.S. Dep. of Agric. For. Serv. Rocky Mt. Res. Station, Fort Collins, Colo.
- Henriksen, A. (1982), Changes in base cation concentrations due to freshwater acidification, acid rain research report, Norw. Inst. for Water Res., Oslo, Norway.
- Henriksen, A., and D. F. Brakke (1988), Increasing contributions of nitrogen to the acidity of surface waters in Norway, *Water Air Soil Pollut.*, 42, 183–201.
- Heuer, K., K. A. Tonnessen, and G. P. Ingersoll (2000), Comparison of precipitation chemistry in the central Rocky Mountains, Colorado, USA, *Atmos. Environ.*, 34, 1713–1722.
- Holt, C., and N. D. Yan (2003), Recovery of crustacean zooplankton communities from acidification in Killarney Park, Ontario, 1971–2000: PH 6 as a recovery goal, *Ambio*, 32, 203–207.
- Hornberger, G. M., B. J. Cosby, and R. F. Wright (1989), Historical reconstructions and future forecasts of regional surface water acidification in southernmost Norway, *Water Resour. Res.*, 25, 2009–2018.
- Jenkins, A., B. J. Cosby, R. C. Ferrier, T. A. B. Walker, and J. D. Miller (1990a), Modelling stream acidification in afforested catchments: An assessment of the relative effects of acid deposition and afforestation, *J. Hydrol.*, 120, 163–181.
- Jenkins, A., P. G. Whitehead, B. J. Cosby, and H. J. B. Birks (1990b), Modelling long-term acidification: A comparison with diatom reconstructions and the implication for reversibility, *Philos. Trans. R. Soc. London, Ser. B*, 327, 435–440.
- Jenkins, A., P. G. Whitehead, T. J. Musgrove, and B. J. Cosby (1990c), A regional model of acidification in Wales, *J. Hydrol.*, 116, 403–416.
- Johannessen, M., and A. Henriksen (1978), Chemistry of snow meltwater: Changes in concentrations during melting, *Water Resour. Res.*, 14, 615–619.
- Kämäri, J., D. S. Jeffries, D. O. Hessen, A. Henriksen, M. Posch, and M. Forsius (1992), Nitrogen critical loads and their exceedance for surface waters, background document, Workshop on Critical Loads of Nitrogen, Løkeberg, Sweden.
- Kelley, T. J., and D. H. Stedman (1980), Effects of urban sources on acid precipitation in the western United States, *Science*, 210, 1043.
- Kendall, C., D. H. Campbell, D. H. Burns, J. B. Shanley, S. R. Silva, and C. C. Y. Chang (1995), Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate, *IAHS Publ.*, 228, 339–347.
- Kratz, K., S. Cooper, and J. Melack (1994), Effects of single and repeated experimental acid pulses on invertebrates in a high altitude Sierra Nevada stream, *Freshw. Biol.*, 32, 161–183.
- Kretser, W., J. Gallagher, and J. Nicolette (1989), *An Evaluation of Fish Communities and Water Chemistry*, Adirondack Lakes Surv. Corp., Ray Brook, N. Y.
- Lafrancois, B. M., K. R. Nydick, B. M. Johnson, and J. S. Baron (2004), Cumulative effects of nutrients and pH on the plankton of two mountain lakes, *Can. J. Fish. Aquat. Sci.*, 61, 1153–1165.
- Landers, D. H., et al. (1987), *Characteristics of Lakes in the Western United States*, vol. 1, *Population Descriptions and Physico-Chemical Relationships*, Rep. EPA/600/3-86/054a, U.S. Environ. Protect. Agency, Washington, D. C.
- Langford, A. O., and F. C. Fehsenfeld (1992), Natural vegetation as a source or sink for atmospheric ammonia: A case study, *Science*, 255, 581–583.
- Lepistö, A., P. G. Whitehead, C. Neal, and B. J. Cosby (1988), Modelling the effects of acid deposition: Estimation of long-term water quality responses in forested catchments in Finland, *Nordic Hydrol.*, 19, 99–120.
- Meixner, T., R. C. Bales, M. W. Williams, D. H. Campbell, and J. S. Baron (2000), Stream chemistry modeling of two watersheds in the Front Range, Colorado, *Water Resour. Res.*, 36, 77–87.

- Munson, R. K., C. T. Driscoll, and S. A. Gherini (1990), Phenomenological analysis of ALSC chemistry data, in *Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984–1987*, pp. 2–27–2–69, Adirondack Lakes Surv. Corp., Ray Brook, N. Y.
- Musselman, R. C., L. Hudness, M. W. Williams, and R. A. Sommerfeld (1996), Water chemistry of Rocky Mountain Front Range aquatic ecosystems, *Res. Pap. RM-RP-325*, Rocky Mt. For. and Range Exper. Stat., Fort Collins, Colo.
- National Acid Precipitation Assessment Program (1991), National Acid Precipitation Assessment Program 1990 integrated assessment report, 520 pp., Washington, D. C.
- Nilsson, J. (Ed.) (1986), Critical loads for sulphur and nitrogen, *Miljørap. 1986:11*, Nord. Counc. of Minist., Copenhagen.
- Nilsson, J., and P. Grennfelt (Eds.) (1988), Critical loads for sulphur and N: Report from a workshop held at Skokloster, Sweden, 19–24 March, *Miljørap. 1988:15*, Nord. Counc. of Minist., Copenhagen.
- Norton, S. A., R. F. Wright, J. S. Kahl, and J. P. Schofield (1992), The MAGIC simulation of surface water at, and first year results from, the Bear Brook Watershed Manipulation, Maine, USA, *Environ. Pollut.*, **77**, 279–286.
- Ollinger, S. V., J. D. Aber, G. M. Lovett, S. E. Millham, R. G. Lathrop, and J. M. Ellis (1993), A spatial model of atmospheric deposition for the northeastern U.S., *Ecol. Appl.*, **3**, 459–472.
- Parrish, D., R. Norton, M. Bollinger, S. Liu, P. Murphy, D. Albritton, and F. Fehsenfeld (1986), Measurements of  $\text{HNO}_3$  and  $\text{NO}_3^-$  particulates at a rural site in the Colorado Mountains, *J. Geophys. Res.*, **91**, 5379–5393.
- Peterson, D. L., and T. J. Sullivan (1998), Assessment of air quality and air pollutant impacts in national parks of the Rocky Mountains and northern Great Plains, *Rep. NPS D-657*, U.S. Dep. of the Int. Natl. Park Serv. Air Resour. Div., Washington, D. C.
- Posch, M., J.-P. Hettelingh, P. A. M. de Smet, and R. J. Downing (1997), Calculation and mapping of critical thresholds in Europe: CCE status report 1997, *RIVM Rep. 25,9101007*, Natl. Inst. for Public Health and the Environ., Githoven, Netherlands.
- Raddum, G. G., and A. Fjellheim (2003), Liming of River Audna, southern Norway: A large scale experiment of benthic invertebrate recovery, *Ambio*, **32**, 230–234.
- Rosenbrock, H. H. (1960), An automatic method for finding the greatest or least value of a function, *Comput. J.*, **3**, 175–184.
- Rueth, H. M., J. S. Baron, and E. J. Allstott (2003), Responses of old-growth Engelmann spruce forests to nitrogen fertilization, *Ecol. Appl.*, **13**, 664–673.
- Sisterson, D. L., V. C. Bowersox, T. P. Meyers, A. R. Olsen, and R. J. Vong (1990), Deposition monitoring: Methods and results, *State Sci. Technol. Rep. 6*, Natl. Acid Precip. Assess. Prog., Washington, D. C.
- Sullivan, T. J. (1991), Long-term temporal changes in surface water chemistry, in *Acid Deposition and Aquatic Ecosystems: Regional Case Studies*, edited by D. F. Charles, pp. 615–639, Springer, New York.
- Sullivan, T. J., and B. J. Cosby (1995), Testing, improvement, and confirmation of a watershed model of acid-base chemistry, *Water Air Soil Pollut.*, **85**, 2607–2612.
- Sullivan, T. J., and B. J. Cosby (1998), Modeling the concentration of aluminum in surface waters, *Water Air Soil Pollut.*, **105**, 643–659.
- Sullivan, T. J., B. J. Cosby, C. T. Driscoll, D. F. Charles, and H. F. Hemond (1996), Influence of organic acids on model projections of lake acidification, *Water Air Soil Pollut.*, **91**, 271–282.
- Sullivan, T. J., J. M. Eilers, B. J. Cosby, and K. B. Vaché (1997), Increasing role of nitrogen in the acidification of surface waters in the Adirondack Mountains, New York, *Water Air Soil Pollut.*, **95**, 313–336.
- Sullivan, T. J., B. J. Cosby, J. A. Bernert, and J. M. Eilers (1998), Model evaluation of dose/response relationships and critical loads for nitrogen and sulfur deposition to the watersheds of Lower Saddlebag and White Dome Lakes, *Rep. 97-10-01*, E&S Environ. Chem., Inc., Corvallis, Oreg.
- Sullivan, T. J., B. J. Cosby, A. T. Herlihy, J. R. Webb, A. J. Bulger, K. U. Snyder, P. F. Brewer, E. H. Gilbert, and D. L. Moore (2004), Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian Mountains, *Water Resour. Res.*, **40**, W02101, doi:10.1029/2003WR001998.
- Sverdrup, H., W. de Vries, and A. Henriksen (1990), Mapping critical loads, report, Nord. Counc. of Minist., Copenhagen.
- Turk, J. T., D. H. Campbell, G. P. Ingersoll, and D. W. Clow (1992), Initial findings of synoptic snowpack sampling in Colorado Rocky Mountains, *U.S. Geol. Surv. Open File*, 92-645.
- U.S. Environmental Protection Agency (1995), Acid deposition standard feasibility study, *Rep. EPA 430-R-95-001A*, Off. of Air and Radiat. Acid Rain Div., Washington, D. C.
- Walthall, P. M. (1985), Acidic deposition and the soil environment of Loch Vale watershed in Rocky Mountain National Park, Ph.D. dissertation, Colo. State Univ., Fort Collins.
- Whitehead, P. G., S. Bird, M. Hornung, B. J. Cosby, C. Neal, and P. Paricos (1988), Stream acidification trends in the Welsh Uplands: A modelling study of the Llyn Brianne catchments, *J. Hydrol.*, **101**, 191–212.
- Williams, M. W., and K. A. Tonnessen (2000), Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA, *Ecol. Appl.*, **10**, 1648–1665.
- Williams, M. W., J. S. Baron, N. Caine, R. Sommerfeld, and R. Senford, Jr. (1996), Nitrogen saturation in the Rocky Mountains, *Environ. Sci. Technol.*, **30**, 640–646.
- Woodward, D. F., A. M. Farag, M. E. Mueller, E. E. Little, and F. A. Vertucci (1989), Sensitivity of endemic Snake River cutthroat trout to acidity and elevated aluminum, *Trans. Am. Fish. Soc.*, **118**, 630–641.
- Wright, R. F., B. J. Cosby, M. B. Flaten, and J. O. Reuss (1990), Evaluation of an acidification model with data from manipulated catchments in Norway, *Nature*, **343**, 53–55.
- Wright, R. F., B. J. Cosby, R. C. Ferrier, A. Jenkins, A. J. Bulger, and R. Harriman (1994), Changes in acidification of lochs in Galloway, southwestern Scotland 1979–88: The MAGIC model used to evaluate the role of afforestation, calculate critical loads and predict fish status, *J. Hydrol.*, **161**, 275–285.

---

D. W. Clow, U.S. Geological Survey, MS 415, Box 25046 Federal Center, Denver, CO 80225, USA. (dwcclow@usgs.gov)

B. J. Cosby, Department of Environmental Sciences, University of Virginia, Charlottesville, VA 22903, USA. (b.j.cosby@virginia.edu)

T. J. Sullivan, E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339, USA. (tim.sullivan@esenvironmental.com)

K. A. Tonnessen, School of Forestry, University of Montana, Missoula, MT 59812, USA. (kathy\_tonnessen@nps.gov)